IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of :
CHARRIERE et al.

US Utility Patent Application No. 09/673,951

Filed: October 24, 2000

For: "METHOD FOR PREPARING LOW VISCOSITY TRICONDENSATE POLYFUNCTIONAL ISOCYANATES"

Group Art Unit: 1711

Examiner: R. Sergent

DECLARATION UNDER 35 C.F.R. § 1.132

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

I, Jean-Marie Bernard, declare as follows:

1) I was awarded a PhD in physicochemistry of biologic and synthetic macromolecules from the Lille 1 University.

2) Currently, I am a Senior staff scientist in Rhodia in the Research Center of Lyon, 85, rue des Frères Perret, BP 62 - F-69192 Saint-Fons Cedex.

3) My Curriculum Vitae, Research Experience and list of publications are attached hereto as Appendix I.

4) I have studied the disclosure no. EP 0 649 866 and I reached the conclusion that the weight % amount (with the understanding of the present invention) of tricondensate allophanates is greater than 10% in each of Examples 2, 3 and 4 of EP 0 649 866. The calculation sheet that allows such assertion is enclosed in Appendix II of the enclosed declaration.

The calculated weight % amount of tricondensate allophanates in each of Examples 2, 3 and 4 is much higher than in the presently claimed invention, which is therefore not anticipated by EP 0 649 866.

5) Under my sup rvision, tests have been conducted in order to provide evidences as to the novelty and non-obviousness of the claimed invention over US 5,258,482 (Jacobs *et al.*) and US 5,235,018 (Potter *et al.*), both references referred to as the "Miles patents" in th following declaration and appendixes. The Miles patents correspond to European patent application no. EP-A-0 524 500.

The annexed results show that the polyisocyanate compositions resulting from the process by Rhodia are different from the compositions resulting from the process disclosed in the Miles patents.

The present invention leads to polyisocyanate compositions of lower viscosity which do not contain or contain only a small amount of isocyanurate – allophanate polyisocyanate structures and for which the NCO function index is higher.

As indicated under the preferred items of the present invention, there indeed exists an optimal alkyl chain length of more or less 8 carbon atoms, for which the HDI and alkyl allophanate presents optimum properties when used as a diluent for polyisocyanates.

I HEREBY DECLARE that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful, false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful, false statements may jeopardize the validity of the application or any patent issued thereon.

Date : 12 janvier 2004

January 12th 2004

Signature : Jean-Marie BERNARD

APPENDIX I

Dr BERNARD, Jean Marie
Born on December 23, 1954 In Somain, France
I studied chemistry and biochemistry in Lille University ("Maîtrise").
In 1981, I graduated as PhD in physicochemistry of biologic and synthetic macromolecules from the Lille 1 University.

Between January 26, 1981 and September 1st, 1986, I worked in the Research Center of the CHOAY Institute (French Pharmaceutical Company) in Paris. During this time, I have been in charge of the synthesis of new active molecules for different therapeutic domains: immunochemistry, heparinotherapy, cardiovascular activity and cancer therapy.
I have acquired an experience in organic chemistry and more specifically in lipid, glycan and peptide chemistry.
I am the author of the following patents and publications on these topics:
- Patents: FR 2551758; FR 2564096; FR 2581069.
- Publications in:
  * J. Biol Response Modif. (1987), 6(6), 678 – 691
  * Int. J . Pept. Prot. Research (1987), 29 (4) 455 – 463
  * J. Biol Response Modif. (1985), 4(5) 464 – 474
  * Peptides Proceedings European, Peptides symposium 18th (1984), 443- 446, Publisher Almquist and Wiksell Stockolm)

From the 1st of September 1986 to mars 1992, I worked in RHÔNE-POULENC as chemical engineer in peptide chemistry and I was in charge of a team (8 members) as technical leader. In mars 1992, I have acquired the function of research associate.
Since 1993, in the Research Center of Lyon (CRL) (RHODIA) and Research Industrialisation and Technology Center (CRIT) of Decines (RHODIA), I am in charge of research of new molecules and new process in the polyisocyanate field for coatings.
I am the author of more than 20 patents in the following different fields: peptide chemistry, organic chemistry and isocyanate chemistry (organic, aqueous and powders compounds and their applications).
I am the author of publications in Synlett (1993) , 9, 680 – 682; Tetrahedron (1994) , 50(2), 497 – 503; Tetrahedron Letters (1994), 35(47), 8783 – 8786; Tetrahedron Letters (1995), 36(8), 1267 – 1270.

I am co-author of the following books:
* "The roots of Organic Development", published in 1996 by ELSEVIER (ISBN no. 0 444 824346 0)
* "Waterborne and Solvent Based Surface Coating Resins and their Applications" published in 1998 by John WILEY and Sons (Chichester / New York / Weinheim / Brisbane / Toronto / Singapore) in association with SITA Technology Ltd (London, UK). (ISBN no. 0471 978868)

I was awarded the RHÔNE-POULENC Research Price in 1991.

I am currently Senior Staff Scientist in the expert file of RHODIA.

- APPENDIX II -

Calculations for the determination of the minimum amount of allophanates present in the prior art (EP 0 649 866)

1- Molecular mass calculations

1-1 DI-isocyanate monomer

di-isocyanate	*formula*	*carbon*	*hydrogen*	*nitrogen*	*oxygen*	*molecular mass*
IPDI	$C_{12}H_{18}N_2O_2$	12	18	2	2	222

1-2 Condensate

condensate	*formula*	*carbon*	*hydrogen*	*nitrogen*	*oxygen*	*molecular mass*
IPDI trimer		36	54	6	6	666
trimer unit		3	0	3	3	126

1-3 Allophanate

allophanate	*formula*	*carbon*	*hydrogen*	*nitrogen*	*oxygen*	*molecular mass*
n-butanol allophanate		28	46	4	5	518

1-4 Mixed: alcohol allophanate and IPDI trimer

alcohol	*formula*	*carbon*	*hydrogen*	*nitrogen*	*oxygen*	*molecular mass*
n-butanol allophanate and IPDI trimer		52	82	8	9	962

2- Calculation of the amounts of tricondensate allophanates (weight %)

	Example 2 of EP 649866	*mass*	*number of moles*	*weight %*
A	IPDI	96.8	0.43603604	
B	butanol	3.2	0.04324324	
C	induced allophanate (1)		0.04324324	
D	remaining IPDI (2)		0.34954955	
E	ratio induced allophanate /(remaining IPDI + induced allophanate)		0.11009174	
F	ratio remaining IPDI /(remaining IPDI + induced allophanate)		0.88990826	
G	allophanate-free trimer /totality of the trimers (3)		0.70475101	
H	trimer units (weight %)	11%		
I	ratio mass of n-butanol allophanate mixed trimer / mass of the trimer unit (962/126)		7.63492063	
J	tricondensate allophanates (weight %) (4)			24.80%

	Example 3 of EP 649866	*mass*	*number of moles*	*weight %*
A	IPDI	96.8	0.43603604	
B	butanol	3.2	0.04324324	
C	induced allophanate (1)		0.04324324	
D	remaining IPDI (2)		0.34954955	
E	ratio induced allophanate /(remaining IPDI + induced allophanate)		0.11009174	
F	ratio remaining IPDI /(remaining IPDI + induced allophanate)		0.88990826	
G	allophanate-free trimer /totality of the trimers (3)		0.70475101	
H	trimer units (weight %)	15%		
I	ratio mass of n-butanol allophanate mixed trimer / mass of the trimer unit (962/126)		7.63492063	
J	tricondensate allophanates (weight %) (4)			33.81%

	Example 4 of EP 649866	*mass*	*number of moles*	*weight %*
A	IPDI	96.8	0.43603604	
B	butanol	3.2	0.04324324	
C	induced allophanate (1)		0.04324324	
D	remaining IPDI (2)		0.34954955	
E	ratio induced allophanate /(remaining IPDI + induced allophanate)		0.11009174	
F	ratio remaining IPDI /(remaining IPDI + induced allophanate)		0.88990826	
G	allophanate-free trimer /totality of the trimers (3)		0.70475101	
H	trimer units (weight %)	13%		
I	ratio mass of n-butanol allophanate mixed trimer / mass of the trimer unit (962/126)		7.63492063	
J	tricondensate allophanates (weight %) (4)			29.30%

(1) = number of moles of alcohol (column B).
(2) = A / 2C.
(3) = F^3 (= F ^ 3).
(4) = (1 - G) * H * I

- APPENDIX III -

Comparison of polyisocyanate compositions of the present invention (Rhodia) and polyisocyanate compositions of the Miles patents

1. Comparison between polyisocyanate compositions obtained from HDI and 1-octanol.

Characteristics	*Example R1 (Rhodia)*[1]	*Example M1 (Miles)*[1]	*Rhodia / Miles ratio*
NCO Index (weight %)	21,4	18	+ 19%
Viscosity (mPa.s) at 25°C	570	830	- 31%
Allophanate / isocyanurate molar ratio[2]	8,2/ 20,8 = 0,395	2,25	
Isocyanurate - allophanate polyisocyanates compounds	0	46,4	

[1] Protocols of the preparation of the Examples compounds are given in Appendix 4
[2] This molar ratio is measured by ^1H NMR analysis (see paragraph 3 below).

It is obvious that the polyisocyanate compositions obtained according to the process by Rhodia from the same starting constituents is different from the composition obtained according to the process by the Miles patents. They possess a high NCO function index (by weight unit) of + 19%, a far lower viscosity (-31%) and does not contain isocyanurate - allophanate polyisocyanate compounds.

From the molar allophanate functions / isocyanurate functions ratio it is clear that, using the process by Rhodia, only a small amount of allophanate diluent is sufficient in order to significantly decrease the viscosity in an important way while preserving a high NCO function index.

It is thereby confirmed that the presence of isocyanurate–allophanate polyisocyanate compounds as obtained using the cited Miles patents is not favorable for the diminishing the viscosity and also that it is preferable that these compounds be absent from low viscosity compositions.

2. Comparison of compositions obtained from HDI and 1-tétradécanol.

Characteristics	*Example R3*	*Example M2*	*Rhodia / Miles ratio*
NCO Index (weight %)	20,9	16,7	+ 25 %
Viscosity (mPa.s) at 25°C	670	905	- 26 %

Characteristics	*Example R3*	*Exampl M2*	*Rhodia / Miles ratio*
Allophanate / isocyanurate molar ratio	0,38	2,2	
Isocyanurate - allophanate polyisocyanates compounds	0	42,6	

From the molar allophanate functions / isocyanurate functions ratio it is clear that, using the process by Rhodia, only a small amount of allophanate diluent is sufficient in order to significantly decrease the viscosity in an important way while preserving a high NCO function index.

The polyisocyanate compositions obtained according to the process by Rhodia possess a high NCO function index (by weight unit) of + 25%, a lower viscosity (-26%) and does not contain isocyanurate - allophanate polyisocyanate compounds.

It is therby confirmed that the presence of isocyanurate–allophanate polyisocyanate compounds as obtained using the cited Miles patents is not favorable for the diminishing the viscosity and also that it is preferable that these compounds be absent from low viscosity compositions.
It is interesting to be noted that the length of the allophanate alkyl chain has a far higher influence on the NCO function index of the compositions of the Miles patents than the one of the compositions by Rhodia.

It is also confirmed that, for the compositions of the present invention, there is an optimum chain length of about 8 carbon atoms for which the viscosity diminution is the highest while preserving a high NCO function index. This is in complete accordance with the preferred items as set forth in the description of the presently claimed invention.

3. Analytical method for the determination of the allophanate / isocyanurate ratios

The analytical method used is proton (^{1}H) NMR, with $CDCl_3$ as solvent.

All HDI species are added, by measuring the four (4) CH_2 signals, between 1.8 and 1.0 ppm, after subtracting the CH_2 values of the alcohol. This measurement is accurate.

The isocyanurate functions are measured from the 3 CH_2–N signal present on the isocyanurate cycle at 3.8 ppm. A slight interference with the signals corresponding to the biuret can be observed at 3.6 ppm. This leads to a less accurate measurement.

The allophanate functions are measured on the basis of the N-H signal at 8.5 ppm. This measurement is fairly accurate.

The allophanate functions / isocyanurate functions ratio is then easily calculated.

Number of functions:

	Sum of the HDI chains	Isocyanurates	Allophanates
Example R1	100	20.8	8.2
Example R2	100	22.1	8.5

- APPENDIX IV -

Examples according to the process by Rhodia

Preparative Example 1 : Preparation of the allophanate of HDI and of 1-octyl

Into a three-necked reactor equipped with a mechanical stirrer and a jacket are charged under nitrogen stream, 840 g of hexamethylene diisocyanate (i.e. 5 moles representing 10 moles of isocyanate functions). The reaction mixture is then heated and 65 g of 1-octanol (0.5 moles representing 0.5 moles of hydroxyl functions) are added. The NCO functions / OH functions molar ratio is therefore 20. The mixture is heated at 100°C for 1 hour, and 0.23 g of dibutyl dilaurate tin (0.025% by weight) are added. The reaction mixture is then heated to 140°C for about 5 hours.

The NCO transformation rate is 13% , i.e. a HDI transformation rate of about 26%.

The reaction mixture is distilled off at 160°C under vacuum (0.2 mm Hg), on a thin film, twice in order to completely eliminate the HDI monomer, the content of which in the final product is less than 0.5%.

247 g of allophanate of HDI and of 1-octyl are collected, the viscosity of which being 85 mPa.s at 25°C, and the NCO index of which being 0.409 mole NCO / 100 g of product, i.e. a weight NCO index of 17,18%.

Yield: 27.3% by weight.

Preparative Example 2 : Preparation of the allophanate of HDI and of 1-butyl

Into a three-necked reactor equipped with a mechanical stirrer and a jacket are charged under nitrogen stream, 840 g of hexamethylene diisocyanate (i.e. 5 moles representing 10 moles of isocyanate functions). The reaction mixture is then heated and 37 g of 1-butanol (0.5 moles representing 0.5 moles of hydroxyl functions) are added. The NCO functions / OH functions molar ratio is therefore 20. The mixture is heated at 100°C for 1 hour, and 0.22 g dibutyl dilaurate tin (0.025% by weight) are added.
The NCO transformation rate is 12.5%.

The reaction mixture is then heated to 140°C for about 5 hours. The reaction mixture is distilled off at 160°C under vacuum (0.2 mm Hg), on a thin film, twice in order to completely eliminate the HDI monomer, the content of which in the final product is less than 0.5%.

230 g of allophanate of HDI and of 1-butyl are collected, the viscosity of which being 105 mPa.s at 25°C, and the NCO index of which being 0.459 mole NCO / 100 g of product, i.e. a weight NCO index of 19.3%.

Yield: 26% by weight.

Preparative Exampl 3 : Preparatl n of the allophanate of HDI and of 1-tetradecanol

Into a three-necked reactor equipped with a mechanical stirrer and a jacket are charged under nitrogen stream, 393 g of hexamethylene diisocyanate (i.e. 2.34 moles representing 4.68 moles of isocyanate functions). The reaction mixture is then heated and 50 g of 1-tetradecanol (0.234 moles representing 0.234 mole of hydroxyl functions) are added. The NCO functions / OH functions molar ratio is therefore 20. The mixture is heated at 100°C for 1 hour, and 0.22 g dibutyl dilaurate tin (0.025% by weight) are added. The reaction mixture is then heated to 140°C for about 5 hours.

The NCO transformation rate is 14.45%, i.e. a HDI transformation rate of 29%. The reaction mixture is distilled off at 160°C under vacuum (0.2 mm Hg), on a thin film, twice in order to completely eliminate the HDI monomer, the content of which in the final product is less than 0.5%.

230 g of allophanate of HDI and of 1-tetradecyl are collected, the viscosity of which being 155 mPa.s at 25°C, and the NCO index of which being 0.354 mole NCO / 100 g of product, i.e. a weight NCO index of 14.86 %.

Example R1

Polyisocyanate composition using allophanate of HDI and of 1-octanol as reactive diluent.

Into a three-necked reactor equipped with a mechanical stirrer are charged under nitrogen 25 g of allophanate of HDI and 1-octyl (Preparative Example 1) and 75 g of TOLONATE® HDT LV (polyisocyanate having a viscosity of 1177 mPa.s at 25°C, a NCO index of 0.544 moles / 100 g and an equivalent weight of 183). Stirring is maintained for 1 hour at room temperature so as to obtain a homogenous product.

The allophanate functions / isocyanurate functions molar ratio, found using the ^1H NMR technique as explained in paragraph 3 above, is of about 0.4 (8.2/20.8 = 0.395).

The viscosity of the obtained polyisocyanate composition is 570 mPa.s at 25°C and the NCO index is 0.510 moles / 100 g, i.e. a NCO index of 21.42%.

A small quantity of allophanate (25 wt%) is sufficient to obtain a two-fold less viscosity for a polyisocyanate.

The above is a clear assessment that the obtained polyisocyanate composition presents a very low viscosity and a high NCO index.

These characteristics are to be compared with the product of the Comparative Example M1 (here below).

Exampl R2

Polyisocyanate composition using allophanate of HDI and of 1-butanol as reactive diluent.

Into a three-necked reactor equipped with a mechanical stirrer are charged under nitrogen 25 g of allophanate of HDI and 1-butyl (Preparative Example 2) and 75 g of TOLONATE® HDT LV (polyisocyanate having a viscosity of 1177 mPa.s at 25°C, a NCO index of 0.544 moles / 100 g and an equivalent weight of 183). Stirring is maintained for 1 hour at room temperature so as to obtain a homogenous product.

The allophanate functions / isocyanurate functions molar ratio, found using the ^1H NMR technique as explained in paragraph 3 above, is of about 0.4 (8.5/22.1 = 0.385).

The viscosity of the obtained polyisocyanate composition is 610 mPa.s at 25°C and the NCO index is 0.522 moles / 100 g, i.e. a NCO index of 21.92%.

A small quantity of allophanate (25 wt%) is sufficient to obtain a viscosity divided by about 2 for a polyisocyanate.

The above is a clear assessment that the obtained polyisocyanate composition presents a very low viscosity and a high NCO index.

Example R3

Polyisocyanate composition using allophanate of HDI and of 1-tetradecanol as reactive diluent.

Into a three-necked reactor equipped with a mechanical stirrer are charged under nitrogen 25 g of allophanate of HDI and 1-tetradecanol (Preparative Example 3) and 75 g of TOLONATE® HDT LV (polyisocyanate having a viscosity of 1177 mPa.s at 25°C, a NCO index of 0.544 moles / 100 g and an equivalent weight of 183). Stirring is maintained for 1 hour at room temperature so as to obtain a homogenous product.

The allophanate functions / isocyanurate functions molar ratio, found using the ^1H NMR technique as explained in paragraph 3 above, is of about 0.4.

The viscosity of the obtained polyisocyanate composition is 610 mPa.s à 25°C at 25°C and the NCO index is 0.497 moles / 100 g, i.e. a NCO index of 20,9 %.

A small quantity of allophanate (25 wt%) is sufficient to ignificantly decrease the viscosity of a polyisocyanate.

The above is a clear assessment that the obtained polyisocyanate composition presents a very low viscosity and a high NCO index.

All the above results are to be compared with Examples M1 and M2 prepared according to the Miles patents as described below.

Preparation of polyisocyanate compositions according to the Miles patents.

The preparation of the isocyanurate - allophanate compounds according to the Miles patents is carried out as stated in the references examples, using hexamethylene diisocyanate (HDI) as the isocyanate monomer and as the alcohols: 1-octanol and 1-tetradecanol.

The catalyst used is a benzyl trimethyl ammonium hydroxide solution at 35% in methanol and diluted to 4.4% in 2-butanol.

Example M1

Preparation of a isocyanurate - allophanate polyisocyanate composition based on HDI and 1-octanol

Into a three-necked reactor equipped with a mechanical stirrer and a jacket are charged under nitrogen stream, 600 g of hexamethylene diisocyanate (i.e. 3.57 moles representing 7.14 moles of isocyanate functions). 47,5 g of 1-octanol (0.357 mole representing 0,357 mole of hydroxyl functions) are added. The NCO functions / OH functions molar ratio is therefore 20. The temperature of the reaction mixture is brought up to 60°C and the alcoholic solution of the benzyl trimethyl ammonium hydroxide is then added. The reaction is exothermic and the temperature of the reaction mixture is maintained between 70 and 90°C.
The cyclotrimerization reaction is allowed to run as long as the transformation rate of isocyanate functions as indicated in the Miles examples is not reached.

As soon as the NCO transformation rate is reached (as measured by dosage according to the said N,N-dibutyl amine method on a sample of the reaction mixture), the reaction is quenched by adding 2-ethyl hexyl phosphate, in an amount equal to the amount of the solution of benzyl trimethyl ammonium hydroxide catalyst.

The reaction mixture is distilled off at 160°C under vacuum (0.2 mm Hg), on a thin film, twice in order to completely eliminate the HDI monomer, the content of which in the final product is less than 0.5%.

340 g of a polyisocyanate composition containing a majority of isocyanurate – allophanate compounds and havinf a viscosity of 830 mPa.s at 25°C, and a NCO index of 0.428 mole NCO / 100 g of product (i.e. a weight NCO index of 18%) are collected. The molar allophanate functions / isocyanurate functions ratio is 2.25.

Example M2

Preparation of a isocyanurate - allophanate polyisocyanate composition based on HDI and 1-tetradecanol

The procedure is the same as for Example M1 above.
The characteristics of the obtained products are presented in the following table.

Analytical results of the isocyanurate-allophanate polyis cyanate compositions prepared acc rding to the pr cess disclosed in th Miles patents

Product/Element	*Example M1*	*Example M2*
Residual HDI	0.07 %	0.05 %
Monocarbamate	0.4 %	
Allophanate of HDI and of 1-octyl or of 1-tetradecyl (and of n-butyl from the catalyst solution)	24.3 %	29.2 %
True trimer	29.3 %	28.2 %
Heavy species containing Isocyanurate – allophanate structures	46.4%	42.6 %
Bis-trimer (presence of allophanate)	10.7 %	9.8 %
Heavy compounds (expressed as tris-trimer) (presence of allophanate)	8.3 %	7.1 %
Other isocyanurate - allophanate species	27.4	25.7
Obtained viscosity (mPa.s)	830	905
NCO index (mole / 100 g)	0.428	0.398
NCO index (wt %)	18%	16.7%
Allophanate functions / isocyanurate functions molar ratio	2.25	2.2
Overall weight yield	53% (340.8 g)	52% (219 g)
NCO transformation rate	32.8	32.2

The process by the Miles patents forms from 24 to 30 % of true allophanate of HDI and of the alcohol involved in the synthesis, but also leads to the formation of a great quantity of isocyanurate - allophanate polyisocyanatates.
The allophanate functions / isocyanurate functions molar ratio confirms the presence of isocyanurate trimer compounds bearing allophanate functions, which compounds are not present in the process of the present invention.

Remarks on the products obtained using 1-octanol.

Considering that the allophanate functions / isocyanurate functions molare ratio is 2.25 (assessed by ^{1}H NMR) and that the theoretical number of moles of allophanate functions is 0.357 (calculated from the amount of alcohol involved in the reaction) and also because no carabamate functions can be found in the reaction mixture, it can be assessed that the number of moles of isocyanurate functions is 0.159.

From the species repartition, it may be estimated that about 70% by weight of the mixture is constituted by molecules having one allophanate function.
The same remark can extend to the products obtained in the Examples involving 1-tetradecanol.